

(19)



JAPANESE PATENT OFFICE

PATENT ABSTRACTS OF JAPAN

(11) Publication number: 10330610 A

(43) Date of publication of application: 15.12.98

(51) Int. Cl

C08L 71/12

C08J 5/16

C08J 5/18

C08L 25/00

F16C 33/20

//(C08L 71/12 , C08L 25:00 , C08L  
53:02 , C08L 23:02 )

(21) Application number: 09139716

(71) Applicant: ASAHI CHEM IND CO LTD

(22) Date of filing: 29.05.97

(72) Inventor: YOSHIDA KAZUO

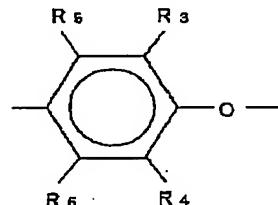
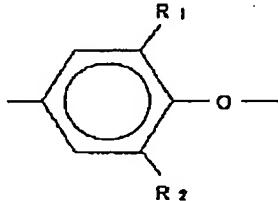
(54) SLIDABLE SHEET ARTICLE

COPYRIGHT: (C)1998,JPO

(57) Abstract:

PROBLEM TO BE SOLVED: To obtain both a thin sheet having excellent heat resistance, sliding resistance and impact resistance and a slidable article, comprising a specific polyphenylene ether-based resin, a polyolefin and a prescribed copolymer.

SOLUTION: This slidable sheet article is obtained by extrusion molding a resin composition comprising (A) 50-85 wt.% of a polyphenylene ether based resin which is composed of a mixture of a polyphenylene ether which is a (co)polymer constituted of a repeating unit of formula I and/or formula II (R<sub>1</sub> to R<sub>6</sub> are each a 1-4C alkyl, an aryl, a halogen or H with the proviso that R<sub>5</sub> and R<sub>6</sub> are not H at the same time) and optionally a styrene resin, (B) 3-20 wt.% of a polyolefin having 130,000 number-average molecular weight and (C) 5-30 wt.% of a hydrogenated block copolymer of a vinyl aromatic compound and a conjugated diene, having 20-40% of bonded amount of the vinyl aromatic compound and ≈150,000 weight-average molecular weight to give a thin sheet and optionally processing the sheet.



**THIS PAGE LEFT BLANK**

# JP 10330610 A

## Disclaimer:

This English translation is produced by machine translation and may contain errors. The JPO, the NCIPI, and those who drafted this document in the original language are not responsible for the result of the translation.

## Notes:

1. Untranslatable words are replaced with asterisks (\*\*\*\*).
2. Texts in the figures are not translated and shown as it is.

Translated: 18:01:59 JST 04/18/2006

Dictionary: Last updated 04/07/2006 / Priority:

---

## CLAIMS

---

### [Claim(s)]

[Claim 1] (a) 50 to 85 weight % of polyphenylene ether system resin which consists of mixture of polyphenylene ether or polyphenylene ether, and styrene resin, (b) In polyolefine, the amount of combination of the (c) vinyl aromatic compound three to 20weight % [ 20 to 40 weight % ] And the sliding nature article with which the hydrogenation block copolymer (HA) of the vinyl aromatic compound and conjugated diene compound which are 150,000 or more weight average molecular weight is obtained by processing the thin meat sheet excellent in the sliding nature which consists of 5 to 30weight % of a resin composition object, and its sheet.

[Claim 2] (d) [ the amount of combination of a vinyl aromatic compound / the hydrogenation block copolymer (HB) of the vinyl aromatic compound and conjugated diene compound which are 40 weight % or more ]. The sliding nature article obtained by processing the thin meat sheet excellent in the sliding nature characterized by consisting of a resin composition object according to claim 1 containing further 3 to 20 weight %, and its sheet.

[Claim 3] The weight average molecular weight of a hydrogenation block copolymer (HA) (c) 200,000 or more (d) The sliding nature article obtained by processing the thin meat sheet excellent in Claim 1 and the sliding nature of two descriptions which consist of the resin composition object characterized by the amount of combination of the vinyl aromatic compound of a hydrogenation block copolymer (HB) being 50 weight % or more, and its sheet.

[Claim 4] The sliding nature article with which thickness is obtained by processing the thin meat sheet excellent in sliding nature. Claim 1 of 1mm or less, 2, and given in three, and its sheet.

---

## DETAILED DESCRIPTION

---

### [Detailed Description of the Invention]

#### [0001]

[Industrial Application] This invention relates to the sliding nature article obtained by processing the thin meat sheet and it of a gel foreign matter excellent in few sliding nature which are excellent in thermal resistance, sliding nature, and shock resistance, and are generally called a fish eye and BUTSU.

#### [0002]

[Description of the Prior Art] Since it excels in a mechanical property, an electrical property, and thermal resistance and absorptivity is low excellent in dimensional stability,

polyphenylene ether is put in practical use by the various application of an industrial component, the electrical and electric equipment and electronic parts, Business Machinery Division, housing, autoparts, a precision component, etc. However, since the polyphenylene ether system resin plasticity object these-put in practical use has the bad self lubricity which can be said also as the fault of amorphous resin and its dynamic friction coefficient is high, it fuses with frictional heat and has the fault which uses as a slide member with parts, such as contact, a revolution, etc. of bearing, a reduction gear, etc., and cannot be used. For this reason, for example, by JP,S50-22040,A, although the proposal which improves sliding nature by adding mineral oil etc. to polyphenylene ether is made, \*\*\*\*\* occurs on the moldings surface and practical use is not borne. Moreover, in JP,S61-185560,A, they are a potassium titanate whisker and powdered high density polyethylene to polyphenylene ether system resin. Although there is a proposal of the purport that the resin composition object for slide members the included constituent excelled [ object ] in abrasion resistance is given, an extreme layer exfoliation phenomenon happens, and also the Plastic solid of the constituent obtained here produces deformation (hollow) in the friction surface after a continuation friction driving test.

[0003] Furthermore, it is in JP,S62-141062,A, The resin composition object which consists of polyphenylene ether system resin and alkyl diphenyl ether is proposed, although lowering of a dynamic friction coefficient and improvement in a limiting PV value are found, there is heat-resistant lowering resulting from an additive, a fusion phenomenon happens during a continuation wear driving test, friction abrasion loss also increases, and practical use is not borne. Furthermore, it is in JP,H4-7357,A and JP,H4-279697,A, Polyphenylene ether, polyolefine with a low dynamic friction coefficient, and Young's modulus of 1500kg/cm<sup>2</sup> as a compatibilizer by controlling the above block copolymer or its hydrogenation object of a vinyl aromatic compound and a conjugated diene compound to a specific distributed form The resin slide member excellent in layer exfoliation, weld strength, and an antifriction and abrasion characteristics is indicated. However, in these invention, although the outstanding sliding effectiveness was demonstrated, to the demand of the high durability nature which has higher shock-resistant reinforcement, it was not enough. Moreover, the extrusion nature in particular of a thin meat sheet of 1mm or less cannot be satisfied, and thickness was not able to obtain the thin meat sheet excellent in thermal resistance and endurance. Furthermore, there was no knowledge for obtaining the thin meat sheet of the high durability nature excellent in thermal resistance, shock resistance, and a sliding characteristic.

[0004]

[Problem(s) to be Solved by the Invention] The technical problem of this invention consists of a polyphenylene ether system resin composition object, and Thermal resistance, It is offering the sliding nature article obtained by processing the thin meat sheet and it which were excellent in sliding-proof nature and shock resistance, and excellent in the sliding nature of high durability nature with few gel foreign matters generally called a fish eye and BUTSU.

[0005]

[Means for Solving the Problem] As a result of inquiring wholeheartedly that this invention persons should attain the above-mentioned object, polyphenylene ether, Polyolefine and the hydrogenation block copolymer of a specific vinyl aromatic compound and a conjugated diene compound are made into a fundamental component. The moldings article with which the resin composition object with which each component consists of a specific ratio was excellent in thin meat sheet extrusion nature with the article, processed the thin meat sheet and it which were obtained, and was obtained found out attaining the above-mentioned technical problem, and resulted in this invention.

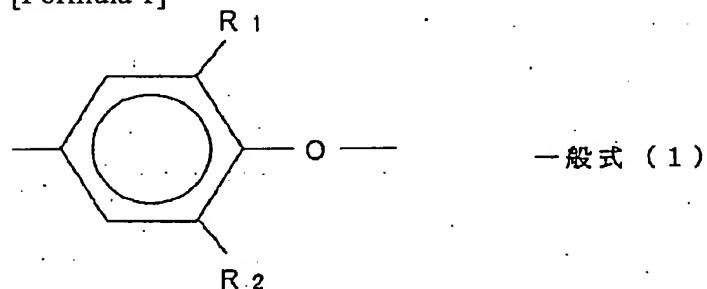
[0006] The mixture which consists of (a) polyphenylene ether or polyphenylene ether, and styrene resin this invention Namely, 50 to 85 weight %, (b) Polyolefine [ 20 to 40 weight % of the amounts of (c) combined styrene ] three to 20weight % And the hydrogenation block

copolymer (HA) of the vinyl aromatic compound and conjugated diene compound which are 150,000 or more weight average molecular weight five to 30 weight % preferably It is the sliding nature article with which the hydrogenation block copolymer (HB) of the vinyl aromatic compound and conjugated diene compound whose amount of combination of the (d) vinyl aromatic compound is furthermore 40 weight % or more is obtained by processing the thin meat sheet excellent in the sliding nature which consists of 3 to 20 weight % of a resin composition object, and its sheet.

[0007] This invention is explained in detail hereafter. The general formula (1) and/or general formula (2) which are indicated below to be (a) polyphenylene ether used by this invention,

[0008]

[Formula 1]



[0009]

[Formula 2]

[0010] (R1, R2, R3, R4, R5, and R6 express the alkyl group of carbon 1-4, an aryl group, a halogen, and hydrogen independently among a formula.) R5 and R6 -- simultaneous -- hydrogen -- it is not -- the homopolymer repeatedly made into a unit or a copolymer can be used. [ however, ] As an example of representation of the homopolymer of polyphenylene ether The Pori (2, 6-dimethyl 1, 4-phenylene) ether, the Pori (2-methyl 6-ethyl 1, 4-phenylene) ether, Pori (2, 6-diethyl 1, 4-phenylene) ETERU, the Pori (2-ethyl 6-n-propyl 1, 4-phenylene) ether, The Pori (2, 6-G n-propyl 1, 4-phenylene) ether, The Pori (2-methyl 6-n-butyl 1, 4-phenylene) ether, The Pori (2-ethyl 6-isopropyl 1, 4-phenylene) ether, Homopolymers, such as the Pori (2-methyl 6-chloro ethyl 1, 4-phenylene) ether, the Pori (2-methyl 6-hydroxyethyl 1, 4-phenylene) ether, and the Pori (2-methyl 6-chloro ethyl 1, 4-phenylene) ether, are mentioned.

[0011] A polyphenylene ether copolymer A copolymer with a copolymer [ of 2 and 6-dimethylphenol and a 2 3, and 6-trimethyl phenol ], copolymer [ with o-cresol ] or 2, 3, and 6-trimethyl phenol, and o-cresol etc., The polyphenylene ether copolymer which becomes considering polyphenylene ether structure as a subject is included.

[0012] Moreover, unless it is contrary to the main point of this invention, the polyphenylene ether of this invention is not cared about even if that you may make it exist in polyphenylene ether conventionally contains other various phenylene ether units proposed as a substructure. Although making it live together in small quantities is proposed, as an example Are indicated to a Japanese-Patent-Application-No. No. 12698 [ 63 to ] gazette, and JP,S63-301222,A. A 2-

(dialkyl aminomethyl)-6-methyl phenylene ether unit, a 2-(N-alkyl N-phenyl aminomethyl)-6-methyl phenylene ether unit, etc. are mentioned. Moreover, what a small amount of diphenoquinone etc. combined in the principal chain of polyphenylene ether is contained. Furthermore, the polyphenylene ether which denaturalized with the compound with the carbon-carbon double bond indicated, for example to JP,H2-276823,A, JP,S63-108059,A, JP,S59-59724,A, etc. is also included.

[0013] The thing of 0.35-0.60 has the desirable intrinsic viscosity measured with the chloroform solution under 30 degrees C, and the polyphenylene ether used for this invention has the more desirable thing of 0.45-0.55. In this invention, it is the range which does not spoil the property of heat-resistant and others, and some polyphenylene ether can be replaced with styrene resin.

[0014] The styrene resin which is mixed with polyphenylene ether as other components which constitute (a) from this invention, and is used is a polymer polymerized and obtained under gum polymer existence or nonexistence in a styrene system compound, a styrene system compound, and a copolymerizable compound. As an example of a styrene system compound, styrene, alpha-methylstyrene, 2, 4-dimethyl styrene, monochlorostyrene, p-methyl styrene, p-tert-butyl styrene, ethyl styrene, etc. are mentioned. moreover, as a styrene system compound and a copolymerizable compound Unsaturated nitrile compounds, such as methacrylic ester; acrylonitrile, such as methyl methacrylate and ethyl methacrylate, and a methacrylonitrile; acid anhydrides, such as a maleic anhydride, etc. are mentioned and it is used with a styrene system compound. 20 or less weight % is desirable still more desirable to the total quantity with a styrene system compound, and the amount of the copolymerizable compound used is 15 or less weight %.

[0015] Moreover, as a gum polymer, a copolymer or ethylene propylene rubber system rubber of conjugated diene system rubber or conjugated diene, and an aromatic vinyl compound etc. is mentioned. Polybutadiene and a styrene butadiene copolymer are especially specifically desirable. Moreover, when using the nature polymer of unsaturated rubber, it is desirable to use the partial hydrogenation rubber-like polymer hydrogenated selectively.

[0016] Especially desirable things are polystyrene and rubber denaturation polystyrene as this styrene resin. The manufacture method of styrene resin of this invention is not limited, and may use any of the bulk polymerization, solution polymerization and emulsion polymerization which are well known to a person skilled in the art, and a suspension polymerization. The number average molecular weight for which (b) polyolefine used by this invention is used as a usual molding material is 30,000 or more polyolefines. For example, high density polyethylene, low density polyethylene, ultrahigh-molecular-weight high density polyethylene, Low density polyethylene, linear low density polyethylene, with a consistency of less than 0.90 ultra low density polyethylene, Isotactic polypropylene, ethylene and a propylene, other alpha olefins, The copolymer of two or more sorts of compounds chosen from unsaturated carboxylic acid or its derivative, For example, ethylene / butene-1 copolymer, an ethylene (meta) acrylic-acid copolymer, an ethylene (meta) acrylic ester copolymer, and a propylene/ethylene (random --) A block copolymer, a propylene / 1-hexene copolymer, a propylene / 4-methyl 1-pentene copolymer and Pori (4-methyl 1-pentene), and polybutene 1 grade can be mentioned, and these can use together not only one sort but two sorts or more. Polyethylene is desirable among such polyolefines and low density polyethylene, linear low density polyethylene, and high density polyethylene are desirable.

[0017] [ the hydrogenation block copolymer of (c) and (d) used by this invention ] The block copolymer which consists of a vinyl aromatic compound and a conjugated diene compound is hydrogenated, and even if there are few olefin nature double bonds based on the copolymerized conjugated diene compound, hydrogenation of the 95% or more is carried out preferably 80% or more. And this rate of hydrogenation can usually be known by an infrared spectrophotometer, NMR, etc. As an example of combination of the polymer block (A) of a

vinyl aromatic compound, and a polymer block (B) of a conjugated diene compound, A-B, A-B-A, A-B-A-B, 4 (A-B), Si, etc. are mentioned.

[0018] As a vinyl aromatic compound which constitutes the block copolymer of a vinyl aromatic compound-conjugated diene compound For example; one sort or two sorts or more can be chosen from among styrene, alpha-methylstyrene, vinyltoluene, p-tertiary butyl styrene, diphenylethylene, etc., and styrene is especially desirable: Moreover, as a conjugated diene compound, one sort or two sorts or more are chosen, for example from among a butadiene, an isoprene, 1,3-pentadiene, 2,3-dimethyl-1,3-butadiene, etc., and a butadiene, isoprenes, and such combination are especially desirable.

[0019] Moreover, 20 to 40weight %, the amount of combined styrene is 30 to 40 weight %, and the weight average molecular weight of the hydrogenation block copolymer (HA) of the (c) vinyl aromatic compound and conjugated diene compound which are used by this invention is 200,000 or more preferably 150,000 or more. Furthermore, the amount of combination of a vinyl aromatic compound is 50 to 90 weight % preferably 40weight % or more, and the weight average molecular weight of the hydrogenation block copolymer (HB) of the (d) vinyl aromatic compound and conjugated diene compound which are used by this invention is 50,000 or more things.

[0020] As long as the hydrogenation block copolymer which these described above has the above-mentioned structure, it may be obtained by what kind of manufacture method. As an example of the well-known manufacture method, for example JP,S47-11486,A, JP,S49-66743,A, JP,S50-75651,A, JP,S54-126255,A, JP,S56-10542,A, JP,S56-62847,A, JP,S56-100840,A, There are a method indicated to the British patent No. 1130770, U.S. Pat. No. 3281383, and 3639517 and a method indicated to the British patent No. 1020720, U.S. Pat. No. 3333024, and 4501857.

[0021] As for the hydrogenation block copolymer, a trade name "tough tech", "Clayton G", "SEPUTON", etc. are marketed, for example. [ the blending ratio of coal of each component of the resin composition object which constitutes fundamentally the article obtained by processing the thin meat sheet of this invention, and its sheet ] The mixture which consists of polyphenylene ether or polyphenylene ether, and styrene resin (a) 50 to 85 weight %, (b) polyolefine 60 to 80weight % preferably 3 to 20 weight %, When (c) hydrogenation block copolymer (HA) is 10 to 25 weight % preferably and uses (d) hydrogenation block copolymer (HB) five to 30weight % five to 15weight % preferably, it is 3 to 20 weight %.

[0022] About an extrusion method, if the aforementioned raw material is used, extrusion molding using the T die usually used in the film of thermoplastics and sheet forming is possible. Although extrusion-molding conditions are suitably chosen by the thermal resistance of a resin composition object and melt viscosity to constitute, as usual extrusion temperature and die temperature, the range of them is 250-350 degrees C. About the structure of a T die, for improvement in the thickness precision of a film or a sheet, a straight manifold or a coat hanger mold manifold is used, and a coat hanger mold is used preferably. Moreover, although a common roll is sufficient as a casting roll, its belt type thing with which two or more rolls were connected by the belt is desirable, and excellent on quality, such as the size enlargement nature of a subsequent thermoforming article, and thickness deviation nature.

[0023] Although the thin meat sheet obtained by extrusion molding can be cut out in desired magnitude and it can also be used as it is Furthermore, the sheet can be fabricated in a desired configuration by thermoforming, such as pressure forming and a vacuum forming, and it can be used for the various sheets with which high heat resistance and high durability nature are demanded and a film, and various heat-resistant tray applications. It is the range which does not spoil the property (balance of thermal resistance, rigidity, the outstanding shock resistance, and sliding nature, generating of BUTSU on a film sheet) of a sheet and mold goods in this invention. Bulking agents, such as fibrous reinforcing agents, such as a plasticizer, a stabilizer, an ultraviolet ray absorbent, a flame retarder, a coloring agent, a

release agent and a glass fiber, and a carbon fiber, and also a glass bead, carbonic acid cull SHUJUMU, and talc, can be added. As a stabilizer, out of phosphite, hindered phenols, alkanolamines, acid amides, dithiocarbamic acid metal salts, inorganic sulfide, and metallic oxides, it is independent, or can combine and blend. Moreover, metal removers, such as lubricant, such as a wax conventionally used as processing aid of resin, and an ultrahigh-molecular-weight polymer, are effective in order to control the poor appearance of improvement in sheet extrusion nature, or a sheet. As other compounding agents, especially combination of conductive carbon black is useful for IC member application.

[0024] Although the heat melting kneading method by a single screw extruder, the twin screw extruder, the roll, the kneader, a Banbury mixer, etc. is mentioned, for example as a method of obtaining the resin composition object which constitutes the thin meat sheet of this invention, the fusion kneading method of having used the twin screw extruder especially is the most desirable. Although the fusion kneading temperature in particular in this case is not limited, it is usually chosen as arbitration in 250-350 degrees C.

[0025]

[The mode of implementation of invention] Hereafter, although an example explains this invention concretely, this invention is not limited to the following examples. The following method estimated the property of the ingredient in an example. Here, about heat deflection temperature and Izod impactive strength, with the thin meat sheet, since it was not able to measure, it measured using the injection-molded product.

1) Heating deformation temperature ASTM It is based on D-648 and they are 18.6kg/cm<sup>2</sup> of loads. It measured.

2) Izod-impactive-strength ASTM It measured based on D-256.

3) Extrusion molding of the 0.15-mm-thick sheet was carried out using the 500-mm-wide T die which adjusted the monopodium sheet extruder of sheet extrusion nature and 40mm of diameters phi of a sheet appearance screw, and the lip crevice to 1.2mm with the cylinder temperature of 300 degrees C of an extruder, and the die temperature of 300 degrees C. On that occasion, the visual judgment of sheet extrusion nature, such as the ease of carrying out of thickness regulation of a sheet and the ease of carrying out of taking over, and the taken-over surface appearance (a fish eye and yield of BUTSU) of a sheet was carried out. as a result, the thing by which the good thing was judged to be O and what inferior was judged to be x and its intermediate level -- \*\* -- it came out and displayed.

4) Attach the pin made of polyethylene terephthalate resin (injection-molded product) by which the radius carried out the form which the flat-surface section of the semicircular pillar with a level die length of 4.5mm attached at 1.25mm at the head of the shape of a cylindrical shape sliding sex-test 5mm in diameter, and 15mm in die length so that a semicircular pillar may touch an extrusion sheet. It pushes against the 0.15-mm-thick extrusion sheet stuck on the movable plate, and a 500g load is applied to the upper part of a pin. Then, friction / wear accelerated test of the pin/plate method which makes 20mm a movable plate reciprocate at 30mm/second in rate was done, and coefficient of friction at the time of the 10000 number of times of a round trip was measured. It excels in sliding nature, so that coefficient of friction is small. as a result, the thing by which the good thing was judged to be O and what inferior was judged to be x and its intermediate level -- \*\* -- it came out and displayed.

5) Use the injection molding machine of 80t of stratified friction test clamping pressure, and it is ASTM at the cylinder temperature of 310 degrees C, and the die temperature of 120 degrees C. The visual judgment of the existence of the stratified exfoliation when pulling, and fabricating and bending a test piece repeatedly at which it applied to D-638 correspondingly was carried out.

[0026] Each component used in the example is as follows.

The intrinsic viscosity which the intrinsic viscosity measured with the chloroform solution under PPE-1:30 degree C measured with the chloroform solution under Pori (2, 6-dimethyl 1,

4-phenylene) ether PPE-2:30 degree C of 0.46 (dl/g) Pori of 0.38 (dl/g) (2, the 6-dimethyl 1, 4-phenylene) Ether PS-1 : Asahi Chemical Industry Co., Ltd. make, Gay polystyrene 685PS-2 : High-impact-polystyrene PE-1 of 12 weight % of rubber contents : Asahi Chemical Industry Co., Ltd. make, Low density polyethylene SANYO ENGINEERING & CONSTRUCTION LD-M1804EP-1 : Hydrogenation object of the product made from Mitsui Petrochemistry, ethylene propylene rubber, and the styrene butadiene block copolymer of a TAFUMA P-0680SEB-1:A-B-A mold. (The weight average molecular weight 240,000, 30 weight % of styrene block content, 99.9% of rate of hydrogenation of the polybutadiene section)

SEB-2: The hydrogenation object of the styrene butadiene block copolymer of an A-B-A-B mold. (The weight average molecular weight 90,000, 60 weight % of styrene block content, 99.9% of rate of hydrogenation of the polybutadiene section)

SEB-3: The hydrogenation object of the styrene butadiene block copolymer of an A-B-A-B mold. (The weight average molecular weight 80,000, 30 weight % of styrene block content, 99.9% of rate of hydrogenation of the polybutadiene section)

SB-1 : Styrene butadiene block copolymer of the 4 (A-B)-Si mold which has not been hydrogenated. (The weight average molecular weight 140,000, 30 weight % of styrene block content)

[0027]

[An example 1-6, a comparative example 1-3] Fusion kneading of the class product shown in a table 1 was carried out at 250rpm with the twin screw extruder of 25mm of diameters of a screw set as 320 degrees C of cylinder temperatures, and the constituent pellet was obtained. Next, the test piece was fabricated for the constituent pellet with the cylinder temperature of 310 degrees C, and the die temperature of 120 degrees C using the injection molding machine of 80t of clamping pressure, and heating deformation temperature and Izod impactive strength were measured.

[0028] The constituent pellet Furthermore, the monopodium sheet extruder of 40mm of diameters phi of a screw, Extrusion molding of the 0.15-mm-thick sheet was carried out using the 500-mm-wide T die which adjusted the lip crevice to 1.2mm with 300 degrees C of cylinder temperatures of an extruder, the die temperature of 300 degrees C, and the roll temperature of about 100 degrees C. An evaluation result is shown in a table 1.

[0029]

[Table 1]

[0030]

[Effect of the Invention] The sliding nature article obtained by processing the thin meat sheet

and it which consist of the specific polyphenylene ether system resin composition object of this invention is useful as various slide members which have a sliding characteristic, the outstanding thermal resistance, and outstanding shock resistance, are excellent also in the surface appearance, and have dynamic contact repeatedly.

---

[Translation done.]